



Matlab Ode Solver for Kinetic Modelling and Simulation of Claus Process Reactions

Ali Abusaloua^{1,*}, Emad Alkhenjari², Muhab Abeid³

¹Department of Chemical Engineering, Faculty of Engineering, Sabratha University, Sabratha, Libya,
ali.abusaloua@sabu.edu.ly

²Department of Chemical Engineering, Faculty of Engineering, Sabratha University, Sabratha, Libya,
emadalkhenjari90@gmail.com

³Department of Chemical Engineering, Faculty of Engineering, Zawia University, Z
Libya, omuhab@gmail.com

ABSTRACT

This paper is focused on a kinetic study and parameter analysis of a chemical reactions in a Claus process of a sulphur recovery unit at Mellita Gas plant. The chemical reactions that take place either in H₂S conversion furnace or in a catalytic converters are studied by an analysis procedures that linked a kinetic modelling to a reactors performance. The kinetic data of a chemical reactions in a Claus process were achieved a ProMax (software) simulator. A PROMAX process simulator is installed and connected to a Distribution Control System (DCS) through instrument analysers and transmitters of a Claus process in a sulphur recovery unit at Mellita Gas plant. A plant kinetic data were used to estimate a reactions parameters by a MATLAB code apply a nonlinear curve fitting regression. The developed kinetic model for a multiple reactions that appear in a several differential equations was implemented and solved numerically by ODE45 solver that available in a MATLAB library. The kinetic model results were visualized and displayed graphically by a MATLAB plot functions.

Keywords:

Clauss process.
Acid gas treatment. Kinetic
modelling.

*Corresponding Author Email: ali.abusaloua@sabu.edu.ly

1 INTRODUCTION

Natural gas is a source of energy, which is widely used as an industrial, commercial, and domestic fuel. To make natural gas suitable for using, it is important to purify it from all impurities such as acid gases. The acid gases of hydrogen sulphide (H₂S) and carbon dioxide (CO₂) are common impurities existing in the natural gas [1].

Acid gas was mainly composed of carbon dioxide (CO₂) and hydrogen sulphide (H₂S). These two problematic compounds must be removed from natural gas in order to appropriate it for further usages as fuel and other applications [2].

Sweetened acid gas, due to stringent environmental regulations must be processed to reduce further hydrogen sulphide. Nowadays, a new technology to convert acid gas to syngas (AG2STM) is proposed [3, 4], but the modified Claus process is still more common than others due to higher sulphur conversion and operation at higher H_2S concentration and capacity [5]. This implies the importance of declaring a kinetic model for its description and optimization of its operation for better performance and higher conversion, consequently lower sulphur dioxide emissions. There are several researchers are developed a kinetic models of a Clauss process multiple reactions in either a thermal furnace or a catalytic reactors. All researchers validate a kinetic model results with industrial experimental data [1-5]. Among the mentioned researchers Pahlavan et al. [2] simulated a Clauss reactions by a PROMAX V2.0 process simulator.

In this study, it is attempted to perform kinetic analysis of clauss process multiple reactions in a thermal furnace of Clauss process of Mellita gas plant. Kinetic analysis consider a simple reaction mechanism include three multiple reactions.

2 MATLAB PROGRAM OVERVIEW:

MATLAB (Matrix Laboratory) is a generalized mathematical software program with many features such as numerical computations, Simulink and control analysis, visualization of results is available from Mathworks [6]

As with any software program, there are few 'rules' and 'codes' which must be followed. The structure of MATLAB consists of M-file or command file type, M-file, there are few general statements to be made about M-file or MATLAB code, is a collection of commands that are executed sequentially, commands can be mathematical operation, function call, flow control statement, and calls to the functions or scripts, the execution of m-file program can be controlled from command file windows or other m-file code. There are two types of m-files, functions and scripts. Function has variables that can passed into and out of the function. Any other variables used inside the function are not saved in memory when the execution of function is finished. Scripts on the other hand, save all their variables in the MATLAB work space. Functions and scripts should be nominated. The first line of a function must contain a function declaration, using a following format:

output Function name [$y_1, y_2, \dots$] = input function name($x_1, x_2, \dots$)

Commented lines immediately following the function declaration and variables nomenclature [7]

2.1 Modelling and simulation in MATLAB

For advanced techniques in modelling and simulation, identification, and control, MATLAB has a variety of tool boxes that are licensed individually. Relevant built in functions for Ordinary Differential Equation (ODE) solver include: several types that are use suitable

numerical technique, Relevant tool boxes for process control include: control system, Fuzzy logic, neural networks, optimization [8]

2.2 Built-in ODE Solvers in MATLAB:

As with most differential equation solvers, there a number of different numerical methods that can be used. Essentially, they are split non-stiff and stiff differential equations. A stiff differential equation is one that has a rapidly varying derivative. That is, the derivative changes rapidly and is therefore susceptible to relatively large errors in the numerical analysis. There are also choices within these two broad categories and these choices are based on the type of errors that can tolerated.

Table1. Ode solvers in a MATLAB library

Stiff ode solvers	Non-stiff ode solvers
Ode15s	Ode45
Ode23s	Ode23
Ode23t	Ode113

The numbers associated with the names indicates the "order" of the numerical method, the "s" indicates the stiff algorithm and the "t" indicates an implementation of the trapezoidal rule. The best bet is to initially try ode45, which utilizes a 4th -5th order Runge-Kutta algorithm. If this takes an unduly long time, then try one of the stiff solvers. If you find that you are having difficulty, the most likely reason is that you have not posed the problem correctly [9].

2.3 MATLAB Method of Lines:

Method of lines is based on the concept of converting the partial differential equation (PDE) into a set of ordinary differential equations (ODE) by discretizing only the spatial derivatives using finite difference and leaving the time derivative unchanged [10].

The method of lines (MOL) is generally recognized as a comprehensive and powerful approach to the numerical solution of time-dependent partial differential equations (PDEs). This method proceeds in two separate steps:

- spatial derivatives are first replaced with finite difference, finite volume, finite element or other algebraic approximations.
- the resulting system of, usually stiff, semi-discrete (discrete in space – continuous in time) ordinary differential equations (ODEs) is integrated in time [11].

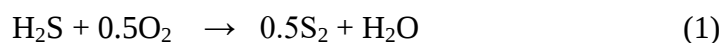
2.4 Model Validation and visualization of Parameters

It easy to visualize and display results in MATLAB graphically. The plot function is used to create simple plots. The command syntax is: plot(x₁,y₁,format1,x₂,y₂,format2,.....), x₁ and x₂ are independent variables (usually time), y₁, y₂ are dependent variables. The format1 and

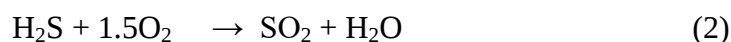
format2 arguments are short combination of characters containing the plot formatted commands [12].

3 CASE STUDY : CLAUS RECOVERY UNIT

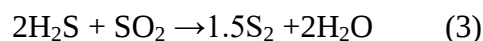
The modified Claus process is one of the major processes which converts toxic hydrogen sulfide to elemental sulfur from acid gas during sour natural gas processing. The modified Claus process in which hydrogen sulfide is converted to sulfur can be depicted by the following simple overall reaction [1]:



The sulfur recovery in the modified Claus process is obtained via the two reaction steps including thermal and catalytic steps. The first step is a thermal step where one third of hydrogen sulfide (H_2S) is partially oxidized and sulfur dioxide (SO_2) is produced at very high temperatures.



The second step involves the reaction between the un-reacted hydrogen sulfide and sulfur dioxide over a catalytic bed at lower temperatures:



Conversion of H_2S to SO_2 in the modified Claus process is conducted in the reaction furnace (RF) which is a refractory lined cylindrical vessel. Since the combustion process in the RF provides substantial sulfur recovery and affects the entire plant emissions, any modification in the RF affects sulfur conversion and emissions from Claus plant. Therefore any improvement in the reaction furnace has direct impact on reduction of sulfur emissions to the atmosphere [14].

3.1 Experimental Data by a PROMAX process simulator:

According to real operation condition in Sulfur recovery unit J_2 , and K_2 at Mellitah complex, the field data have been collected from transmitters and analyzers in distribution control system (DCS). Nowadays, simulation software is one of the most powerful tools in improving the operating conditions of industrial units. it is necessary to improve these software packages or use a better method. Environment has an essential role in Claus unit and its performance affects process efficiency and other equipment performance, so, in the current work, SRU simulation is discussed. Many useful softwares have been improved to study chemical and petroleum industry in terms of the process modelling and simulation, these softwares can be used to simulate the oil and gas processing to enhance the process operation

and increase the productivity. ProMax and Aspen HYSYS are the most common used software. ProMax has been used as a simulator in this research. It is a powerful engineering simulation software, designed with respect to the program architecture, interface, engineering capability and interactive operation, therefore, ProMax process software is known as one of the best process simulation software. It applies the conception of fluid package that contains all the required data and information to perform chemical and physical properties calculation, therefore, ProMax property is the driver of the process and it must be chosen carefully by allowing the definition of all the information such as property package, components, hypothetical components, interaction parameters, reactions, etc. [15].

Development Of a Reactor Model

Partial differential equations(PDE) play an important role in the mathematical modelling of a biological, physical, or chemical systems. Many engineering problems involve diffusion and reaction processes. These problems include the diffusion of pollutants into the air, water and earth. Each area has its own physics, chemistry, biology and ecology. The modelling of these areas often leads to a partial differential equations (PDE). Such equations may be linear, in which the analytical solutions is often achievable. However, many of diffusion and reaction problems are non-linear and numerical solutions are used to solve and understand these models [16].

There has been a considerable amount of research devoted to developing numerical techniques for solving boundary value problems (PDE) in the chemical engineering literature. The large

size of this body of literature reflects the prevalence of (PDE) in chemical process modelling involve diffusion and reaction where their parameter distribution defined on finite domain [17].

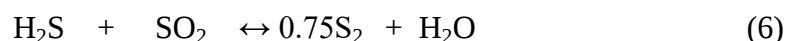
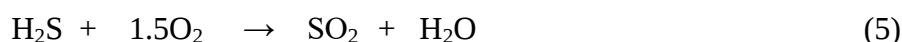
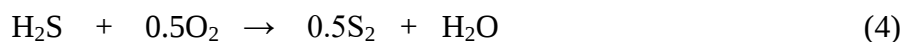
Multiple reactions system consisting of a parallel or series reactions that takeplace simultaneously. The development of reactor modelling for multiple reactions need to follow the steps of kinetic analysis that originally published by Fogler [18] and presented below.

Steps of analyzing multiple reactions:

- Number each rxn.
- . Write the mole balances for each species.
- . Determine the rate law for each species in each reaction.
- . Relate the rate of reaction of each species to the species for which the rate law is given for each reaction.
- . Determine the net rate of formation of each species.

- . Express rate laws as a function of concentration ,C_j, for the case of no volume change.
- . Express rate laws as a function of moles, N_j(batch), or molar flow rates, F_j(flow) when these volume change with reaction.
- . Combine all of the above and solve the resulting set of coupled differential equations (P.F.R, P.B.R, Batch) or (CSTR)

The mathematical manipulations translate the multiple reactions by applying basic of chemical reaction kinetics to translate a multiple reactions equations to ordinary differential equations(ODE) that can be solved numerically by a MATLAB ode solver [18]. In this research, the reactor modelling of a reactor furnace was analysed by considering adiabatic plug flow, and the pressure drop is neglected, Consider the following set of reactions [20]:



For simplicity the components in the previous set of reactions is renamed as, A,B, C,....., the new set of reactions is written as:



Write a relative rate of reaction for each component in each reaction by applying the general rule that shown below as:

$$\frac{r_1\text{A}}{-a_1} = \frac{r_1\text{B}}{-b_1} = \frac{r_1\text{C}}{-c_1} = \frac{r_1\text{D}}{-d_1} \quad (10)$$

The relative of reaction for 1st reaction is written as:

$$\frac{r_1\text{A}}{-1} = \frac{r_1\text{B}}{(-0.5)} = \frac{r_1\text{C}}{0.5} = \frac{r_1\text{D}}{1} \quad (11)$$

For 2nd reaction as:

$$\frac{r_2\text{A}}{-1} = \frac{r_2\text{B}}{-1.5} = \frac{r_2\text{E}}{1} = \frac{r_2\text{D}}{1} \quad (12)$$

For 3rd reaction as:

$$\frac{r_3\text{A}}{-1} = \frac{r_3\text{E}}{-0.5} = \frac{r_3\text{C}}{0.75} = \frac{r_3\text{D}}{1} \quad (13)$$

The general reaction rate expression for selected component of known frequency factor and activation energy are written as:

$$r_{H_2S} = K_1 \cdot \exp(-E_1/R.T) \cdot P_{H_2S} \cdot P_{SO_2}^{0.5} - k_2 \cdot \exp(-E_2/RT) \cdot P_{H_2O} \cdot P_{S_2}^{0.75} \quad (14)$$

$$r_{O_2} = K_1 \cdot \exp(-E_1/R.T) \cdot P_{H_2S} \cdot P_{O_2}^{1.5} \quad (15)$$

$$r_{S_2} = K_1 \cdot \exp(-E_1/R.T) \cdot C_{H_2O} \cdot C_{S_2}^{0.75} - K_2 \cdot \exp(-E_2/R.T) \cdot C_{H_2S} \cdot C_{O_2}^{0.5} \quad (16)$$

the final rate expressions of the chosen kinetic mechanism after manipulation with the relevant rate of reaction are shown below.

$$1- \quad r_{1A} = r_{H_2S} = K_1 \cdot \exp(-E_1/R.T) \cdot P_{H_2S} \cdot P_{SO_2}^{0.5} - k_2 \cdot \exp(-E_2/RT) \cdot P_{H_2O} \cdot P_{S_2}^{0.75}$$

$$E_1=49.4\text{J/mol} \quad E_2= 44.9\text{J/mol} \quad K_1 = 1.75 \cdot 10^7 \text{mol/m}^3\text{sec} \quad K_2 = 5 \cdot 10^5 \text{mol/m}^3\text{.sec}$$

$$R=8.314 \text{ (J/mol K)} \quad T= 1273\text{K}$$

$$2- \quad r_{2B} = r_{O_2} = K_1 \cdot \exp(-E_1/R.T) \cdot P_{H_2S} \cdot P_{O_2}^{1.5}$$

$$R=8.314 \text{ (J/mol K)} \quad T= 1273\text{K} \quad K_1 = 21 \text{mol/m}^3\text{.sec} \quad E = 11\text{J/mol}$$

$$3- \quad r_{3C} = r_{S_2} = K_1 \cdot \exp(-E_1/R.T) \cdot C_{H_2O} \cdot C_{S_2}^{0.75} - K_2 \cdot \exp(-E_2/R.T) \cdot C_{H_2S} \cdot C_{O_2}^{0.5}$$

$$R=8.314 \text{ (J/mol K)} \quad T= 1273\text{K} \quad K_1 = 23310 \text{mol/m}^3\text{.sec}$$

$$K_2 = 2.385 \cdot 10^6 \text{mol/m}^3\text{.sec} \quad E_1 = 8.5\text{J/mol} \quad E_2 = 14.3\text{J/mol}$$

Kinetic Parameter Estimation

In a non-linear least square analysis, searching for a parameter values that minimize the sum of square of the differences between the measured values and predicted values for all the data points [19]. MATLAB software is used to illustrate this technique for a claus process reactions in sulphur recovery unit at Mellia gas plant.

4 RESULTS AND DISCUSSION

Numerical Solution

MATLAB have a high performance and flexibility for numerical computations and results visualisations. There are several ordinary differential equation solver (ODE) in MATLAB program library. The developed kinetic model of differential equations (one per each component) were implemented and solved using ODE45 MATLAB SOLVER that constructed based on four point Ruge-Kuta numerical technique coupled with a method of lines. The MATLAB code was developed by using scripts and built in functions. Figure 1 shows the flow chart of numerical solution algorithm for reactor model

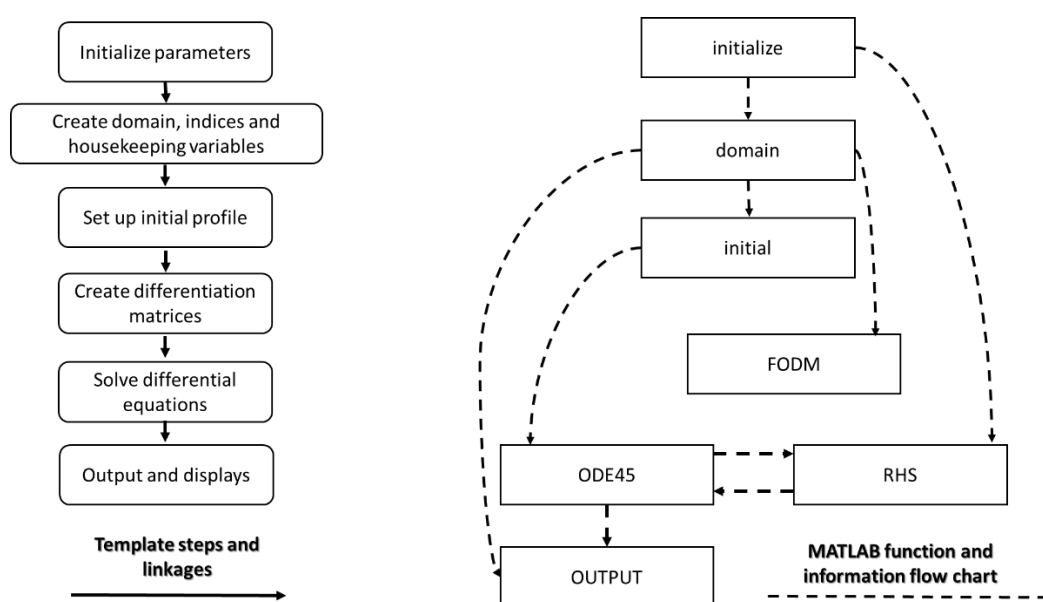


Figure 1. The flow chart of numerical solution algorithm for reactor model

For a nonlinear regression of kinetic data to estimate the reactions parameters, MATLAB code is written by minimizing principles of objective function. Figure 2. Shows the flow chart of MATLAB code of parameter estimation.

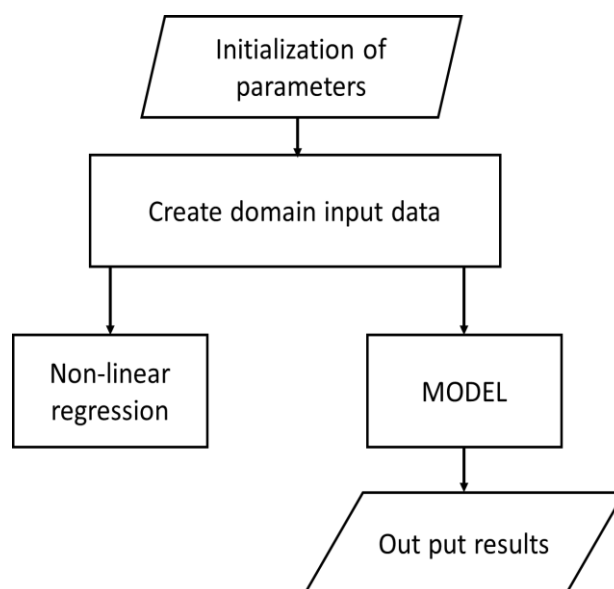


Figure 2. The flow chart of MATLAB code of parameter estimation.

In this work, the influence of air flow rate is studied, by solving a kinetic model for combustion of hydrogen sulphide in a furnace. A typical trend in the time of concentration of residual hydrogen sulphide, intermediates, and carbon dioxide is shown in Figure 3.

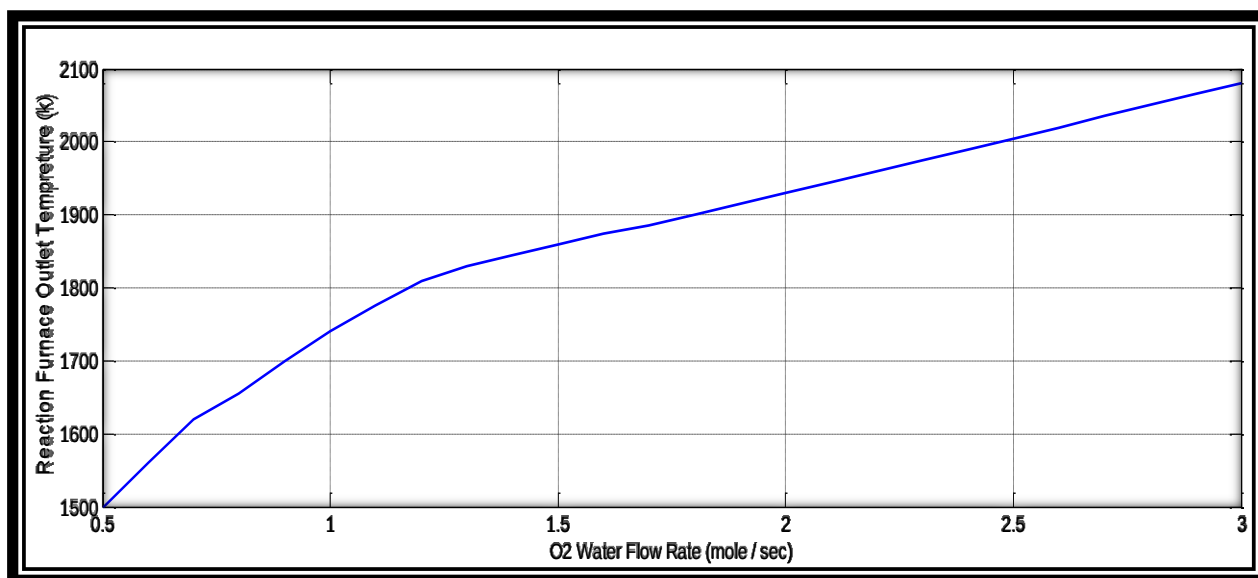


Figure 3. Reaction Furnace Outlet Temperature Vs Water Flow Rate

As can be seen in Figure 4, the H_2S concentration decreased since this compound was adsorbed and transformed to intermediate products.

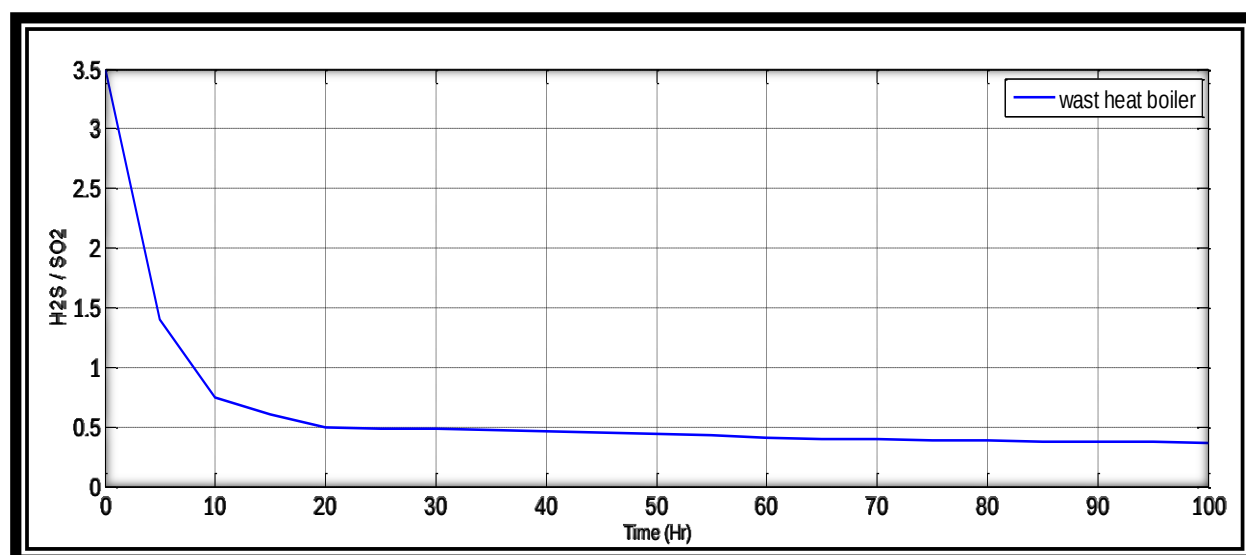


Fig 4. H_2S/SO_2 Vs Time

In Figure 5, is shown a plot of hydrogen sulphide and sulphate dioxide ratio. it can be noticed from these two figures 4 and 5, their concentrations reaches a maximum at the beginning and then decreased. The time needed to reach a maximum and then decreased is faster during a period of several hours simulation.

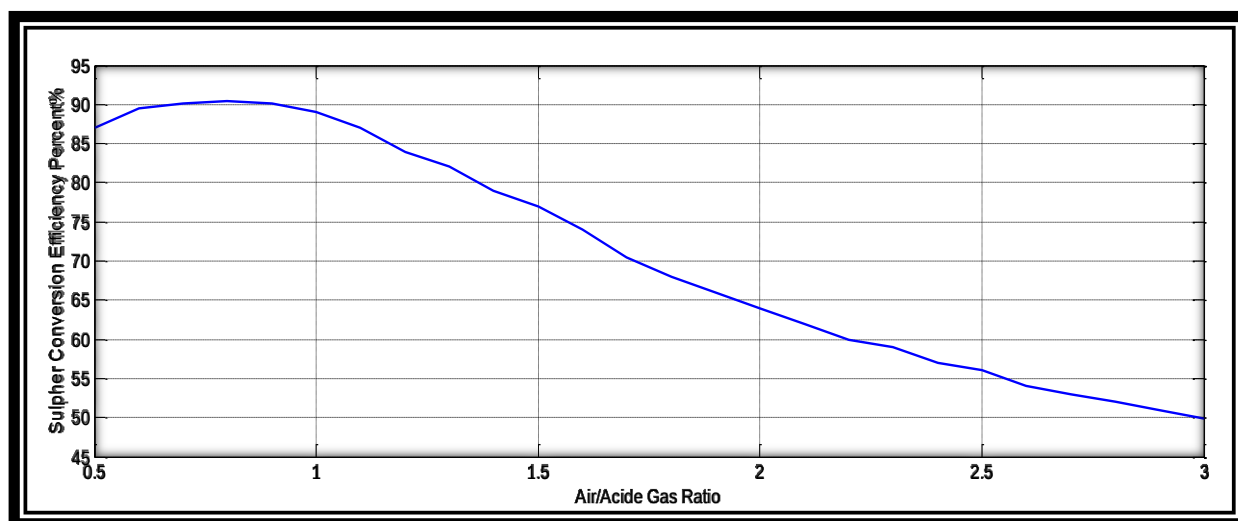


Figure 5. The Sulphuro Conversion Efficiency Percentage

5 DISCUSSION AND CONCLUSIONS

The results of simulated model are shown in Figures 3 through 5. It is seen from these figures, as expected for this case study, that after long enough time, H_2S is consumed and then transformed into intermediate compounds and final products, the rest of compounds satisfy the equilibrium condition at different periods of time.

The air to acid gas flow ratio, initial feed temperature, and steam pressure in the WHB are operating variables that can be changed in operating Claus furnace in order to maintain H_2S/SO_2 ratio to maximize sulfur conversion efficiency

In this paper, kinetic modelling and multiple reaction analysis were applied for Clauss process multiple reactions. Clauss process is used to treatment of acid gases by reducing its concentration before it released to the atmosphere.

The ordinary differential equations of a kinetic model of Clauss process multiple reactions is solved numerically by ode45 solver that available in a MATLAB library. The numerical solution was implemented in a MATLAB code by coupling ode45 solver with a method of lines technique. The visualisation of a kinetic model results is shown in graphical representation by a MATLAB plot functions.

The numerical solution results showed a logical trend concentration of hydrogen sulphide.

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استعمال منسق ODE في برنامج الماتلاب للنمذجة الحركية ومحاكاة تفاعلات عملية كلاوس

علي أبوصلوة¹، عماد الخنجاري²، مهاب عبيد³

¹قسم الهندسة الكيميائية، كلية الهندسة، جامعة صبراتة، صبراتة، ليبيا، ali.abusaloua@sabu.edu.ly

²قسم الهندسة الكيميائية، كلية الهندسة، جامعة صبراتة، صبراتة، ليبيا، emadalkhenjari90@gmail.com

³قسم الهندسة الكيميائية، كلية الهندسة، جامعة الزاوية، الزاوية، ليبيا، omuhab@gmail.com

الملخص

يركز هذا البحث على دراسة حركية الجزيئات وتحليل المتغيرات لتفاعلات كيميائية في عملية كلاوس لوحدة استخلاص الكبريت في مصنع مليته للغاز. تتم دراسة التفاعلات الكيميائية التي تحدث إما في فرن تحويل كبريتيد الهيدروجين أو في المحولات الحفازة من خلال إجراءات التحليل التي تربط النمذجة الحركية بأداء المفاعلات. البيانات الحركية للتفاعلات الكيميائية في عملية كلاوس تم تحقيقها باستعمال برامج المحاكاة كمحاكي ProMax (برمجي). يتم تثبيت محاكي عملية PROMAX وتوصيله بنظام التحكم في التوزيع (DCS) من خلال أجهزة تحليل خاصة وأيضاً أجهزة الإرسال لعملية Claus في وحدة استرداد الكبريت في مصنع مليته للغاز. تم استخدام البيانات الحركية للوحدة الصناعية لتقدير معاملات التفاعلات بواسطة كود MATLAB الذي يطبق انحدار منحني غير خطي مناسب. تم تنفيذ النموذج الحركي المطور لتفاعلات متعددة تظهر في عدة معادلات تفاضلية وحلها عددياً بواسطة محلل ODE45 المتوفر في مكتب MATLAB. تم تصور نتائج النموذج الحركي وعرضها بيانياً بواسطة وظائف رسومات برنامج MATLAB.

الكلمات الدالة:

عملية كلاوس.

معالجة الغاز الحامضي.

النمذجة الحركية.

*البريد الإلكتروني للباحث المراسل: ali.abusaloua@sabu.edu.ly